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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the manufacturing method of the acrylic polymer which does not use a solvent substantially. This invention relates to the method of advancing a polymerization reaction stably, in more detail, without [without it uses a solvent substantially, and] making it react out of control using a pyrolysis type polymerization initiator.

[0002]

[Description of the Prior Art] The acrylic system monomer has good polymerization nature. It can polymerize by various reaction methods, such as solution polymerization, suspension polymerization, an emulsion polymerization, photopolymerization method, and the UV polymerizing method.

For example, the mixture of an acrylic system monomer and mercaptans is heated to the temperature within the limits of 20-200 ** under existence of oxygen as a method of manufacturing an acrylic polymer, The method (refer to JP,50-401,B) and acrylic system monomer which perform mass polymerization, and mercaptans are included, How to polymerize the mixture which does not contain an initiator substantially under a nitrogen atmosphere (and) [patent No. 258251-gazette-] The method (refer to JP,2-55448,B) and batch type reacting can which polymerize in a high temperature region (about 150 **) not using a batch type reacting can but using extrusion type barrel equipment are irradiated with UV light with an optical fiber, The method (refer to JP,11-49811,A) of carrying out UV mass polymerization, etc. are proposed changing reaction temperature gradually irradiating with UV the method (refer to JP,7-330815,A) and batch type reacting can which are polymerized by the pulse irradiation of UV light.

[0003] However, such an acrylic system monomer, Since reactivity is high, even if you are going to make it react in the batch type reacting can of existing of an industrial scale using a

pyrolysis type polymerization initiator, While generation of heat in a reaction apparatus was intense, it was difficult to remove this reaction fever out of the system of reaction and it controlled the reaction effectively using the pyrolysis type polymerization initiator in the reacting can, mass polymerization of the acrylic system monomer was not able to be carried out.

[0004]It is necessary to set reaction temperature as a high temperature region, and there is a problem that the molecular weight of the polymer obtained by the molecular weight distribution of the polymer obtained becoming large in connection with the accuracy of temperature control becoming low probably becomes powder in the reaction using a barrel type device. In the barrel type device using a UV irradiation device, temperature control is difficult and highly precise reaction control cannot be performed. In the batch type reacting can which formed the UV irradiation device, great cost starts the cooling equipment for controlling generation of heat accompanying scale-up, and the method of producing an acrylic polymer in large quantities using an existing facility is not turned to.

[0005]By the way, the mass polymerization using an acrylic system monomer, From a solvent not containing in the generated polymer and a surface-active agent etc. not containing in the polymer generated further. Since other ingredients like the surface-active agent which becomes the cause of not needing separating operation, such as a solvent from the generated polymer, and reducing the characteristics, such as a water resisting property, easily are not contained, if it sees from the gestalt of a reaction, it will be a desirable reaction gestalt.

[0006]However, in the mass polymerization using a pyrolysis nature polymerization initiator, since the reactivity of the monomer used is high, it is very difficult to control a thermal polymerization reaction, and easy to produce a reckless run of a polymerization reaction. A run away reaction has the tendency for the molecular weight of the polymer obtained from states -- reaction temperature rises quickly -- changing from a reaction being uncontrollable quickly by being dramatically dangerous and the molecular weight distribution of the polymer to generate becoming large to also become low.

[0007]About the mass polymerization method using such an acrylic system monomer, to JP,53-2589,A. (Meta) Polymerize a mixture or syrup and acrylic ester and a cross-linking formation monomer are faced manufacturing thermosetting acrylics, Conversion manufactures not less than 60% of precuring object at the temperature of 150 ** or less first, this is taken out from a tank reactor, and the manufacturing method of the thermosetting acrylics which polymerizes at the multistage polymerization process set up so that a conversion difference might be 10 to 60% about this precuring object is indicated. And in the example shown in this gazette, azobisisobutyronitrile, about 0.01-0.3 weight sections of tert-butylperoxy laurate, etc. are used to monomer 100 weight section. 10 hour half life period temperature of this azobis butyronitrile is 66 **, If 10 hour half life period temperature of tert-butylperoxy laurate is 98.3 **

and a pyrolysis type polymerization initiator with 10 hour half life period temperature high in this way is used in the quantity of about 0.01-0.3 weight sections to a monomer as mentioned above, If the temperature of the system of reaction rises quickly and does not use a highly efficient cooling system simultaneously with a reaction start, a reaction will run recklessly. Therefore, it is necessary to advance a polymerization reaction in multistage, fully cooling so that a reaction may not run recklessly at each process using the reaction apparatus provided with the cooling system which has refrigeration capacity sufficient in the invention of a statement in this gazette. For this reason, in a method given in this gazette, in order to cool the system of reaction, highly efficient equipment is needed.

[0008]To JP,58-87171,A. The 1st step that the half-life at 70 ** is [step] 0.1 to 1000 hours, and the half-life at an initial temperature of a polymerization carries out [step] 0.00005-0.5 weight-section use of the radical polymerization initiator of 0.1 to 5 hours to 100 weight sections at an acrylic monomer, and polymerizes an acrylic monomer at 40-120 **, Half-life [in / the half-life at 70 ** is longer than 1000 hours, and / an initial temperature of a polymerization] carries out 0.0001-1 weight-section addition of the radical polymerization initiator which is 2 hours or more, The method of manufacturing the acrylic pressure sensitive adhesive of the weight average molecular weight 100,000-600,000 which consists of the 2nd step polymerized at the temperature of 100-200 ** more highly than the 1st step is indicated. And as a polymerization initiator currently used by the invention given [this] in a gazette, Acetyl peroxide, lauroyl peroxide, benzoyl peroxide, Diisopropyl peroxide, di-2-ethylhexylperoxycarbonate, tert-butylperoxy (2-ethylhexanoate and tert-butylperoxy laurate.) Azo compounds, such as organic peroxide [, such as tert-butylperoxy acetate], azobisisobutyronitrile, 2, and 2'-azobis (2,4-dimethylvaleronitrile), are illustrated.

[0009]Although the polymerization initiator currently used by the invention given [this] in a gazette is a thermal polymerization initiator, 10 hour half life period temperature is within the limits of 43-102 **, and there is no selectivity in 10 hour half life period temperature of the thermal polymerization initiator currently used by this thermal polymerization initiator. Rather, that amount used characterizes the statement about the polymerization initiator in this gazette, and it is indicated that it can be used so much from using a thermal polymerization initiator in small quantities dramatically. Even if such a thermal polymerization initiator tends to be used and it is going to control reaction temperature at 40-120 **, it originates in the activity of the reactional initiator to be used, and the calorific value also differs remarkably. For example, when tert-butyl peroxide, benzoyl peroxide, etc. which are used in the example are used. Since the temperature of the system of reaction rises steeply simultaneously with the start of a reaction, in order to suppress such generation of heat, there is a problem of needing a very highly efficient cooling system.

[0010]The monomer mixture which makes methyl methacrylate the patent No. 2752458

gazette with the main ingredients is taught to a complete-mixing type reactor, The dissolved oxygen in a monomer shall be 1 ppm or less, and the half-life at polymerization temperature uses the radical polymerization initiator for 0.5 to 120 seconds, Stirring by specific stirring force, mean residence time is set up so that the half-life and mean residence time of a radical polymerization initiator may become within the limits of specification, and the manufacturing method of the methacrylic system polymer polymerized so that a monomer inversion rate may be 45 to 70% at the temperature within the limits of 130-160 ** is indicated.

[0011]And the radical polymerization initiator currently concretely used in the example indicated in this gazette, It is 2,2-azobisisobutyronitrile, tert-butylperoxy iso butyrate, lauroyl peroxide, etc., and 10 hour half life period temperature exceeds 41 **. For this reason, for example by an example and drawing 2, in order to suppress a run away reaction, such as using the heat exchange apparatus cooled with a -5 ** refrigerant as a cooling system, the very highly efficient cooling system is used.

[0012]Thus, in the conventional mass polymerization method, the method of there being no technical idea of choosing the polymerization initiator to be used, conveying the generated heat out of the system of reaction using a highly efficient cooling system, and inhibiting a run away reaction was adopted. Therefore, in such a method, there is a problem that a cooling system becomes very expensive. In manufacture of the acrylic polymer of an industrial scale in which a reaction does not advance easily uniformly, If it is dramatically difficult to cool the whole reaction tank uniformly and a reaction runs recklessly in the part in a reaction apparatus even if it uses a considerably highly efficient cooling system, the run away reaction, There is a possibility of affecting the whole system of reaction, and it cannot be adapted as it is in the industrial manufacturing method in scale-up in the reaction which advances stably on a laboratory level.

[0013]

[Objects of the Invention]In the mass polymerization method, an object of this invention is to provide the method of advancing stably, without making a reaction run recklessly. When especially this invention manufactures an acrylic polymer on a scale of industrial, it relates to the method that a reaction can be advanced stably without making a reaction run recklessly.

[0014]

[Summary of the Invention]This invention is the method of carrying out mass polymerization of the monomer which has a polymerization nature unsaturated bond which uses acrylic alkyl ester as the main ingredients, As opposed to monomer 100 weight section in which 10 hour half life period temperature has the above-mentioned polymerization nature unsaturated bond for a polymerization initiator 41.0 ** or less, Add in a quantity of 0.0001 to 0.5 weight section within the limits, make it start, and the polymerization reaction of the monomer which has this polymerization nature unsaturated bond after a reaction start, It is the method of making the

maximum temperature of a reactant reaching the temperature within the limits of 100-140 **, and polymerizing 15 to 50% of the weight of the monomer which has the this used polymerization nature unsaturated bond using self-generation of heat of this system of reaction by this polymerization initiator being consumed.

[0015]This invention is the method of carrying out mass polymerization of the monomer which has a polymerization nature unsaturated bond which uses acrylic alkyl ester as the main ingredients, As opposed to monomer 100 weight section in which 10 hour half life period temperature has the above-mentioned polymerization nature unsaturated bond for a polymerization initiator 41.0 ** or less, Add in a quantity of 0.0001 to 0.5 weight section within the limits, make it start, and the polymerization reaction of the monomer which has this polymerization nature unsaturated bond after a reaction start, After making the maximum temperature of a reactant reach the temperature within the limits of 100-140 ** using self-generation of heat of this system of reaction by this polymerization initiator being consumed, by the cooling operation which adds this monomer that carries out a polymerization nature unsaturated bond. It is the method of polymerizing 15 to 50% of the weight of the monomer which has the polymerization nature unsaturated bond which quenched the temperature of this reactant at less than 100 **, and was used for this polymerization.

[0016]After the above-mentioned polymerization initiator is consumed and the temperature of the system of reaction becomes lower than 100 ** in this invention, As opposed to monomer 100 weight section which has a polymerization nature unsaturated bond to which further 10 hour half life period temperature remains a polymerization initiator 41.0 ** or less in the system of reaction, Add in a quantity of 0.0001 to 0.5 weight section within the limits, prepare reaction mixture again, make it start again, and a polymerization reaction after a reaction start, The maximum temperature of the system of reaction is made to reach the temperature within the limits of 100-140 ** using self-generation of heat of this system of reaction by this polymerization initiator being consumed, It is preferred to perform operation of polymerizing further 15 to 50% of the weight which doubled the monomer which has this polymer and a polymerization nature unsaturated bond of gross weight, once [at least].

[0017]Thus, since a polymerization initiator is extremely consumed for a short time by using a little polymerization initiators with 10 low hour half life period temperature, the mass polymerization reaction of this invention advances, without running recklessly. And conversion can be eventually made not less than 95.0% by repeating such a reaction.

[0018]

[Detailed Description of the Invention]Next, the mass polymerization method of this invention is explained concretely. By the method of this invention, the monomer which has a polymerization nature unsaturated bond is used as a monomer. The monomer which has this polymerization nature unsaturated bond can use acrylic alkyl ester as the main ingredients,

and can mention the compound shown below as an example of the monomer which has such a polymerization nature unsaturated bond.

[0019]Methyl acrylate, ethyl acrylate, acrylic acid propyl, butyl acrylate, Acrylic acid pentyl, acrylic acid hexyl, acrylic acid-2-ethylhexyl, Acrylic acid alkyl ester like acrylic acid octyl, acrylic acid nonyl, decyl acrylate, and acrylic acid dodecyl; Acrylic acid phenyl, Acrylic acid aryl ester like acrylic acid benzyl; Acrylic acid methoxy ethyl, Acrylic acid ethoxyethyl, acrylic acid propoxyethyl, acrylic acid butoxyethyl, acrylic acid alkoxy alkyl; like acrylic acid ethoxypropyl -- salt [, such as acrylic acid and acrylic acid alkali metal salt,]; -- salt [, such as methacrylic acid and methacrylic acid alkali metal salt,]; -- methyl methacrylate. Ethyl methacrylate, methacrylic acid propyl, butyl methacrylate, Methacrylic acid pentyl, methacrylic acid hexyl, methacrylic acid-2-ethylhexyl, Methacrylic acid alkyl ester; methacrylic acid phenyl like methacrylic acid octyl, methacrylic acid nonyl, methacrylic acid decyl, and methacrylic acid dodecyl, methacrylic acid aryl ester like benzyl methacrylate; Methacrylic acid methoxy ethyl, Methacrylic acid ethoxyethyl, methacrylic acid propoxyethyl, methacrylic acid butoxyethyl, Methacrylic acid alkoxy alkyl like methacrylic acid ethoxypropyl; Diacylic ester of ethylene glycol, Diacylic ester of a diethylene glycol, diacylic ester of triethylene glycol, Diacylic ester of a polyethylene glycol, diacrylic acid SL of propylene glycol, Diacrylic acid SL of dipropylene glycol, diacylic ester of alkylene glycol like diacylic ester (poly) of tripropylene glycol; Dimethacrylate ester of ethylene glycol, Dimethacrylate ester of a diethylene glycol, dimethacrylate ester of triethylene glycol, diacylic ester of a polyethylene glycol, methacrylic acid SL of propylene glycol, dimethacrylate ester of dipropylene glycol, Like dimethacrylate ester of tripropylene glycol. (Poly) Dimethacrylic acid ester [of alkylene glycol]; trimethylolpropane -- doria -- multivalent acrylic ester; like krill acid ester -- multivalent methacrylic-acid-ester; like trimethylolpropane TORIMETA krill acid ester -- acrylonitrile; -- methacrylonitrile; -- vinyl acetate;. Vinylidene chloride; Acrylic acid-2-chloroethyl, vinylic halide compound; like methacrylic acid-2-chloroethyl -- acrylic ester [of alicyclic alcohol like acrylic acid cyclohexyl]; -- methacrylic-acid-ester [of alicyclic alcohol like cyclohexyl methacrylate]; -- 2-vinyl-2-oxazoline. An oxazoline group content polymerization nature compound like 2-vinyl-5-methyl-2-oxazoline and 2-isopropenyl-2-oxazoline; An acryloyl aziridine, A methacryloyl aziridine, acrylic acid-2-aziridinylethyl, An aziridine group content polymerization nature compound like methacrylic acid-2-aziridinylethyl; Allyl glycidyl ether, acrylic acid glycidyl ether, methacrylic acid glycidyl ether, acrylic acid glycidyl ether, An epoxy group content vinyl monomer like acrylic acid-2-ethyl glycidyl ether and methacrylic acid-2-ethyl glycidyl ether; Acrylic acid-2-hydroxyethyl, Methacrylic acid-2-hydroxyethyl, acrylic acid-2-hydroxypropyl, Monoester with acrylic acid or methacrylic acid, a polypropylene glycol, or a polyethylene glycol, A hydroxyl content vinyl compound like an addition with lactone and acrylic acid (meta)-2-hydroxyethyl; Fluoride substitution methacrylic acid alkyl ester, Fluorine-containing vinyl monomers, such as fluoride substitution acrylic acid alkyl ester; (meta).

Remove acrylic acid. Itaconic acid, crotonic acid, maleic acid, unsaturated carboxylic acid like fumaric acid, These salts, these (portion) ester compounds, and an acid anhydride; 2-KURORU ethyl vinyl ether, A reactant containing halogen vinyl monomer like monochloro vinyl acetate; Amide group content vinyl monomer; vinyltrimetoxysilane like methacrylamide, N-methylolemethylacrylamide, N-methoxy ethylmethacrylamide, and N-butoxymethylmethacrylamide, Gamma-methacryloxpropyl trimethoxy silane, allyl trimethoxysilane, Trimethoxysilylpropyl allylamine, an organic silicon group content vinyl compound monomer like 2-methoxyethoxy trimethoxysilane; in addition to this, The macro monomers (for example, a fluorine system monomer, a silicon content monomer, a macro monomer, styrene, silicon, etc.) which have a radical polymerization nature vinyl group at the monomer end which polymerized the vinyl group can be illustrated.

[0020]these polymerization nature unsaturated compounds are independent -- it is -- it can be combined and used. On a reaction condition, although the monomer which has these polymerization nature unsaturated bonds may be a fluid, may be a solid and may be a gas, it is preferred to use the monomer which is a fluid from the simplicity of operation in the case of a reaction. Even if reaction velocity is high also especially in the above compounds and it is a monomer which cannot carry out mass polymerization easily, mass polymerization can be stably performed by adopting the method of this invention. For example, also in the combination of a monomer with high reaction velocity, the method of this invention can be effectively used like the mixture of 2-ethylhexyl acrylate and acrylic acid. Although there is no restriction in particular in the content of the acrylic alkyl ester in the monomer which has a polymerization nature unsaturated bond used in the mass polymerization method of this invention, in the method of this invention. It is suitable for especially carrying out mass polymerization of the monomer which contains acrylic alkyl ester in a quantity of one to 100 weight section within the limits suitably 0.1 to 100 weight section into total monomers (inside of 100 weight sections).

[0021]The monomer which has the above-mentioned unsaturated bond is made to react in the method of this invention, without using a reactional solvent substantially. In the method of this invention, the monomer which has the above-mentioned unsaturated bond is polymerized using a specific polymerization initiator. In this invention, 10 hour half life period temperature uses the polymerization initiator which is within the limits of 20-37.0 ** preferably 41.0 ** or less as a polymerization initiator.

[0022]As an example of such a polymerization initiator, isobutyryl peroxide (10 hour half life period temperature: 32.7 **), alpha and alpha'-bis(neo decanoyl peroxy)diisopropylbenzene (10 hour half life period temperature: 35.9 **), Cumil peroxy neodecanoate (10 hour half life period temperature: 36.5 **), Di-n-propyl peroxy dicarbonate (10 hour half life period temperature: 40.3 **), Diisopropyl peroxy dicarbonate (10 hour half life period temperature: 40.5

**), Di-sec-butyl peroxydicarbonate (10 hour half life period temperature: 40.5 **), 1, 1, 3, 3, - tetramethyl butylperoxyneodecanoate (10 hour half life period temperature: 40.7 **), Bis(4-butylcyclohexyl)peroxy dicarbonate (10 hour half life period temperature: 40.8 **) and 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (10 hour half life period temperature: 30.0 **) can be mentioned.

[0023]they are polymerization initiator independent [these] -- it is -- it can be combined and used. Also in these, isobutyryl peroxide (10 hour half life period temperature: 32.7 **), alpha and alpha'-bis(neo decanoyl peroxy)diisopropylbenzene (10 hour half life period temperature: 35.9 **), Cumil peroxy neodecanoate (10 hour half life period temperature: 36.5 **), It is preferred to use 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (10 hour half life period temperature: 30.0 **), Especially the thing for which 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (10 hour half life period temperature: 30.0 **) is used is preferred.

[0024]The above-mentioned polymerization initiator is a thermal polymerization initiator, and, moreover, the 10 hour half life period temperature is remarkably low. For example, 10 hour half life period temperature of tert-butylperoxy isobutyrate which is the polymerization initiator currently generally used from the former is 72.1 **, 10 hour half life period temperature of benzoyl peroxide is 74 **, and 10 hour half life period temperature of 2,2'-azobisisobutyronitrile is 66 **. In [if a thermal polymerization initiator with such 10 high hour half life period temperature is used] a mass polymerization reaction, A reaction advances quickly from immediately after a reaction start, and in this invention which becomes very difficult, control of a reaction advances a polymerization reaction using a little thermal polymerization initiators with it rather than uses a thermal polymerization initiator with the 10 above high hour half life period temperature. [10 remarkable hour half life period temperature and] [low]

[0025]That is, in this invention, within the limits of 0.0005 to 0.1 weight section uses [within the limits of 0.0001 to 0.5 weight section] such a polymerization initiator in a quantity of 0.001 to 0.05 weight section within the limits still more preferably to monomer 100 weight section which has a polymerization nature unsaturated bond. The amount of such polymerization initiator used in this invention is very little as compared with the amount of the reactional initiator used in the usual mass polymerization etc.

The quantity of the monomer which reacts with this polymerization initiator is little, and that polymerization calorific value is less than the quantity of heat emitted from the system of reaction.

Therefore, after heating the system of reaction first, for example and making a reaction start, operation of applying heat to this system of reaction from the exterior is not usually performed. If a reaction is started, in this system of reaction, will generate heat by consuming the above-mentioned polymerization initiator, but. In this invention, since there is little amount of the polymerization initiator used, the temperature of the system of reaction does not rise rapidly,

so that a reaction runs recklessly few as for the calorific value, If a polymerization initiator is dramatically consumed for a short time from using a polymerization initiator with 10 low hour half life period temperature, the temperature of a reactant will rise steeply and all polymerization initiators will be consumed, the temperature of a reactant will not rise any more. If the quantity of a polymerization initiator deviates from the above-mentioned lower limit greatly, with the polymerization inhibitor which usually contains the monomer which is a raw material so that a reaction may not advance during storage etc., a polymerization initiator will be consumed and a polymerization reaction will not advance effectively.

[0026]And after a reaction start makes the maximum temperature of a reactant within the limits of 100-140 ** reach the temperature within the limits of 100-130 ** preferably using self-generation of heat of this system of reaction by this polymerization initiator being consumed, and is kept from exceeding the maximum of this temperature requirement. usually, heating after heating in order to start a polymerization reaction or warming -- using self-generation of heat accompanying suspending operation and a polymerization reaction advancing -- the temperature of the system of reaction -- the range of 100-140 ** -- within the limits below not less than 100 ** 130 ** is made to reach preferably In the method of this invention, in particular after a reaction begins to advance, it is not necessary to carry out heating or cooling but, and it does not eliminate heating or cooling so that the maximum temperature of the system of reaction may be carried out into a mentioned range.

[0027]If the temperature of the system of reaction exceeds 140 **, a reckless run of the reaction by thermal polymerization will start, and it will become difficult to control this thermal run-away reaction. If a maximum temperature is less than 100 **, a polymerization cannot be advanced to desirable conversion by this mass polymerization reaction, an initiator remains to the system of reaction and there is a problem of a polymerization advancing during storage of a reactant. In manufacture with a factory level on which especially reaction raw materials exceed 1000 kg when the scale of a reaction becomes large, If the usual cooling system was used when the temperature of the system of reaction became close to 150 **, It is almost difficult to stop a reckless run of a reaction, and if are not based on the method of throwing in a lot of polymerization inhibitor, and it becomes difficult to suspend a run away reaction and reaction temperature exceeds 180 ** further, this run away reaction cannot stop. Namely, if a polymerization initiator with 10 high hour half life period temperature which is used conventionally is used, At the temperature of 100-140 **, it will become impossible for an initiator not to be consumed thoroughly but for the temperature of the system of reaction to rise, and for thermal polymerization to newly advance, and for the temperature of the system of reaction to rise further, and to control a reaction by the rise in heat of this system of reaction finally. It is a reckless run of the reaction in mass polymerization.

[0028]Raise the temperature of the system of reaction quickly within the limits of 100-140 **,

mainly using the reaction fever produced by the polymerization reaction triggered by using a little polymerization initiators with 10 low hour half life period temperature of 41.0 ** or less in this invention, and a polymerization initiator is made to consume for a short time, a reaction maximum temperature -- a reaction -- it has controlled at controllable 140 ** or less.

[0029]And the short thing of time to hold the highest arrival temperature of such a reaction within the limits of 100-140 ** in this invention is preferred, and the highest arrival temperature of a reaction is usually maintained for [30 seconds -] 2 minutes in a mentioned range in the method of this invention. The time when the highest arrival temperature is maintained in the above-mentioned temperature requirement is much less than the above-mentioned minimum, if short, a polymerization reaction may not advance effectively, and it far exceeds the above-mentioned maximum, and when long, the thermal polymerization thing which is not preferred may arise.

[0030]Thus, the partial polymer in which 15 to 50% of the weight of the monomer used as a raw material polymerized in one polymerization reaction which carries out a little polymerization initiators chosen [above-mentioned] can be obtained. And by adding a new polymerization initiator and repeating this process, By 15 to 50% of the weight which united the polymer's and the monomer's which has a polymerization nature unsaturated bond's in each stage of quantity reacting, and repeating such operation, It is possible to polymerize at least 95.0% of use monomers eventually, and according to the method of this invention, it becomes possible to polymerize all mostly about the used monomer. And since it goes on under mild conditions, like the output of the mass polymerization which ran recklessly, the reaction in each process has not been said that much polymer of a short chain occurs, and can manufacture the uniform polymer to which the molecular weight was equal.

[0031]in the method of this invention, when a polymerization initiator is blended, a monomer is heated or warmed to the temperature to which a polymerization reaction may advance, and the above-mentioned regulation of the above-mentioned predetermined reactional initiator is carried out into this monomer -- quantity addition is carried out and a polymerization reaction is advanced. The temperature of the monomer at the time of adding a polymerization initiator has especially usual [20-80 ** of / 35-70 ** of] within the limits of 40-65 ** preferably. In this way, a polymerization initiator is usually added under stirring at the monomer heated or warmed.

[0032]Although the above-mentioned example is an example which heats a monomer and adds a polymerization initiator, it can perform mixing with this monomer and polymerization initiator, and heating in arbitrary order. For example, after mixing a monomer and a polymerization initiator, it can also heat to the temperature by which a reaction is started, and addition mixing of the postpolymerization initiator which heated the monomer as mentioned above to the temperature by which a reaction is started can also be carried out.

[0033]As for the cooking temperature of a monomer required for making a polymerization

reaction start effectively in the method of this invention, usual [20-80 ** of / 35-70 ** of] is 40-65 ** especially preferably. By heating to such a temperature, a polymerization initiator acts effectively and the polymerization reaction of the method of this invention begins to advance effectively at first. In this way, since a polymerization initiator decomposes continuously, a reaction advances and the temperature of the system of reaction becomes at a stretch within the limits of 100-140 ** once a polymerization reaction begins, As long as the polymerization initiator which in the usual case does not need to heat or warm after a reaction start, and is specified by this invention is used according to regulation of this invention, since the maximum temperature does not exceed 140 **, it does not in particular need cooling. however, heating operation for this invention to adjust the temperature of the system of reaction in such a stage and warming -- temperature-control operation of operation or cooling operation is not eliminated.

[0034]In this way, if a polymerization reaction begins and a reaction begins in this way, the temperature of the system of reaction will rise steeply by self-generation of heat. And if the highest arrival temperature will be 100-140 **, since the added polymerization initiator is consumed nearly thoroughly, the calorific value accompanying advance of a reaction will fall and the direction of the heat release from the system of reaction will become large. Therefore, more, if the temperature of the system of reaction does not rise but is neglected as it is, the temperature of the system of reaction will become lower than 100 **. Although the reactant attained to the maximum temperature can be neglected and it can also cool in this invention, Once it is preferred to make temperature of the system of reaction lower than 100 ** as much as possible in this invention for a short time, for this reason the temperature of the system of reaction reaches even a maximum temperature, Can also use the cooling system formed in the reaction apparatus, and, Or can also adopt the method of adding the monomer which is not heated to the system of reaction, and making temperature of the system of reaction (monomer web thinning) lower than 100 ** for a short time, and. Temperature can also be made the system of reaction by publicly known cooling operation or means, such as combining both, at 100 ** or less. It is preferred to use the monomer contained in that system of reaction for monomer web thinning, and the quantity of the monomer used in this case is usually 20 to 30 weight section preferably ten to 50 weight section to monomer 100 weight section taught first.

[0035]By making it react in this way, the partial polymerization syrup in which 15 to 50% of the weight of the preparation monomer polymerized is obtained. Thus, the partial polymerization syrup obtained is usually obtained as a 1-500-poise consistency fluid (it measures using 23 ** and a Brookfield viscometer). In the method of this invention, after cooling the partial polymerization syrup produced by performing it above in temperature of [below 100 **], it can add in small quantities, and can mix so that 10 above-mentioned hour half life period temperature may specify a polymerization initiator 41.0 ** or less by this invention, and

operation of heating again and making a polymerization resuming can be performed. By repeating this operation, the conversion of partial polymerization syrup can become high gradually, and can polymerize the monomer of ** 95.0% of the weight or more by the method of this invention eventually.

[0036]In this way, the partial polymerization syrup (partial polymer, or eventually polymer) obtained by polymerizing in multistage, By the viscosity's becoming high whenever it repeats the above-mentioned process, for example, performing the above-mentioned operation once, the viscosity will usually be about 5 times - about 10 times to the viscosity of the raw material before performing the operation, and the content of the residual monomer in a reactant falls.

[0037]Although specific amount use of the monomer which has a polymerization nature unsaturated bond as mentioned above, and the specific polymerization initiator is carried out in the polymerization method of this invention, It is preferred to use together a chain transfer agent still like normal dodecyl mercaptan, butyl mercaptan, 3-mercaptopropionic acid, thioglycolic acid, and thioglycolic acid ester in this invention. Such a chain transfer agent is usually preferably used in a quantity of 0.01 to 0.5 weight section within the limits 0.001 to 10 weight section to monomer 100 weight section to be used.

[0038]It is preferred to perform a polymerization reaction under stirring in the method of this invention, and it is preferred to perform a reaction under inert atmospheres, such as nitrogen gas. Since the oxygen dissolved in a use raw material may bar advance of a reaction, it is preferred to use it in advance of the method of this invention, after removing the dissolved oxygen in a use raw material. Since according to the method of this invention a little specific polymerization initiators with 10 low hour half life period temperature are used and 100-140 ** of maximum temperatures of a reactant are preferably controlled mainly using the heat of polymerization to within the limits below not less than 100 ** 130 **, It can react on mild conditions, without a reaction running recklessly also in mass polymerization.

[0039]

[Effect of the Invention]The method of this invention is the method of carrying out mass polymerization of the monomer which has a polymerization nature unsaturated bond, and a little polymerization initiators whose 10 hour half life period temperature is very low are used, After starting the polymerization reaction by this polymerization initiator, it is the method of making the maximum temperature of the system of reaction reaching 100-140 ** at a stretch, mainly using the reaction fever accompanying advance of this exoergic reaction, and polymerizing 15 to 50% of the weight of the monomer which consumed the added polymerization initiator and was used. Thus, the method of this invention can perform mass polymerization, without making it run recklessly, without using the conventional device as it is and moreover performing cooling and heating operation by polymerizing out of various polymerization initiators by choosing the polymerization initiator of 10 specific hour half life

period temperature, in the usual case.

[0040]

[Example] Next, this invention is not limited by these, although an example is shown and this invention is explained still in detail.

[0041]

[Example 1] An agitator, a thermometer, a nitrogen gas introducing pipe, and a condenser tube in a 4 mouth flask with a capacity of 0.2 l. which it had 92 g of 2-ethylhexyl acrylate (2-EHA), Acrylic acid (AA) Temperature up was carried out and heating was suspended until it supplied 8 g and 0.06 g of normal dodecyl mercaptan and became 50 ** in the nitrogen air current.

[0042] Subsequently, it supplied as a polymerization initiator under stirring of 0.0025 g of 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (inside of 10 hour half life period temperature of 30 ** / toluene), and mixed uniformly. After carrying out polymerization initiator addition, the rise in heat by the heat of polymerization was seen 3 minutes afterward by continuing stirring, but the temperature of the system of reaction amounted to 118 ** by keeping generated heat, without cooling a flask and making it react. By furthermore continuing stirring, the polymerization initiator added to the system of reaction was consumed, the rise in heat of the system of reaction beyond this was not seen, and a reckless run of the reaction was not seen. About this reactant, when the polymerization initiator was analyzed, it was checked that the whole quantity of the added polymerization initiator had been deactivated.

[0043] as a cooling agent, 2g of AA (23g and 25 **) is added for 25 ** 2-EHA -- it carried out, and the temperature of the system of reaction was quenched to 100 ** or less using the external cooler, external intercooling was continued succeedingly, and partial polymerization syrup was obtained. The amount of polymer of this obtained partial polymerization polymerization syrup is 28%.

It was consistency resin liquid whose viscosity is 50 poise.

[0044]

[Comparative example 1] In Example 1, although it tried to perform a polymerization reaction similarly except having changed the amount of the polymerization initiator used into 0.00005 g, even if 30 minutes passed, reaction mixture did not generate heat, and the polymerization reaction did not advance.

[0045]

[Comparative example 2] In Example 1, except having changed the amount of the polymerization initiator used into 2 g, when a polymerization reaction is performed similarly, the temperature of the reactant in a flask reaches at a stretch to 154 **, and temperature is continuing rising further gradually. When the temperature of the reactant amounted to 180 **, continuation of the reaction beyond this judged that it fell into reaction loss of control, threw in

reaction inhibitor, and stopped the reaction compulsorily.

[0046]

[Comparative example 3] In Example 1, 10 hour half life period temperature as a polymerization initiator instead of the 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) which is 30 **, Except 10 hour half life period temperature having used the 2 and 2'-azobisiso butyronate tolyl which is 66 **, when a polymerization reaction is performed similarly, the temperature of the reactant in a flask reaches at a stretch to 158 **, and temperature is continuing rising further gradually. When the temperature of the reactant amounted to 180 **, continuation of the reaction beyond this judged that it fell into reaction loss of control, threw in reaction inhibitor, and stopped the reaction compulsorily.

[0047]

[Comparative example 4] In Example 1, 10 hour half life period temperature as a polymerization initiator instead of the 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) which is 30 **, Except 10 hour half life period temperature having used the benzoyl peroxide which is 74 **, when a polymerization reaction is performed similarly, the temperature of the reactant in a flask reaches at a stretch to 166 **, and temperature is continuing rising further gradually. When the temperature of the reactant amounted to 180 **, continuation of the reaction beyond this judged that it fell into reaction loss of control, threw in reaction inhibitor, and stopped the reaction compulsorily.

[0048]

[Comparative example 5] In Example 1, although similarly polymerized except not having used 25 ** 2-EHA and 25 ** AA, for 20 minutes was taken to cool the temperature of a reactant at less than 100 **, the thermal polymerization reaction advanced in the meantime, and the viscosity of the reactant became high. The obtained partial polymer was consistency resin liquid with a viscosity of 74 poise 30% by polymer.

[0049]

[Example 2] After cooling the partial polymerization syrup obtained in Example 1 to 50 ** with an external-intercooling device and monomer web thinning in a nitrogen air current, 0.005 g of 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) was supplied, and it mixed uniformly. After carrying out polymerization initiator addition, the rise in heat by the heat of polymerization was seen 3 minutes afterward by continuing stirring, but the temperature of the system of reaction amounted to 117 ** by keeping generated heat, without cooling a flask and making it react. By furthermore continuing stirring, the polymerization initiator added to the system of reaction was consumed, the rise in heat of the system of reaction beyond this was not seen, and a reckless run of the reaction was not seen. About this reactant, when the polymerization initiator was analyzed, it was checked that the whole quantity of the added polymerization initiator had been deactivated.

[0050]as a cooling agent, 2g of AA (23g and 25 **) is added for 25 ** 2-EHA -- it carried out, and the temperature of the system of reaction was quenched to 100 ** or less using the external cooler, external intercooling was continued succeedingly, and partial polymerization syrup was obtained. The amount of polymer of this obtained partial polymerization polymerization syrup is 50%.

It was consistency resin liquid whose viscosity is 310 poise.

[Translation done.]